EVALUATION OF NITROGEN RELEASE CHEMISTRY USING DETAILED CHEMICAL STRUCTURAL CHAR DATA

S. T. Perry and T. H. Fletcher

Department of Chemical Engineering Brigham Young University, Provo, Utah 84602

Keywords: coal, pyrolysis, ^{13}C NMR, nitrogen

Introduction

Nitrogen release from coal during devolatilization is difficult to predict due to coal to coal variations. Two computer models for prediction of nitrogen release from coal during devolatilization have been proposed (Bassilakis et al., 1993; Niksa, 1995). Parameters in these models were tuned by matching predicted nitrogen release to light gas and tar nitrogen from various coals with experimentally measured values. Both models use a distributed activation energy first-order rate expression, with one or two coal-dependent parameters, which are then correlated to the ultimate analysis of the coal. The chemistry responsible for the variations in nitrogen release with coal type is not well understood, and therefore is only treated empirically in these models. These models are based on the following assumptions:

1. All fuel-bound nitrogen atoms are distributed randomly within the aromatic nuclei in the coal.
2. During tar release, tar aromatic nuclei "shuttle" nitrogen atoms contained therein to the tar product, in an amount proportional to the number of aromatic nuclei in the tar.
3. During primary devolatilization, the aromatic nuclei/aromatic rings are conserved within the pyrolysis products, that is, ring condensation and opening reactions are negligible, except for HCN production.
4. During devolatilization, the rate of release of nitrogen atoms from the aromatic nuclei can be described as a first order process with a distributed activation energy.

Based on these assumptions, the model proposed by Niksa (1995) predicts the nitrogen release as light gas based on changes in the ratio of moles of nitrogen to moles of aromatic nuclei (η_0). Alternatively, changes in the ratio of mass of nitrogen to mass of aromatic carbon ($R_{N\text{-}AC}$) can be used to predict light gas nitrogen release, the two variables differing only by a conversion factor:

$$R_{N-AC} = \left(\frac{MW_C}{MW_N} \cdot AC_{cl} \right) \eta_0 \qquad (1)$$

where MW_C and MW_N are the atomic weights carbon and nitrogen, respectively, and AC_{cl} is the number of moles of aromatic carbons per mole of aromatic clusters or nuclei. Alternatively, $R_{N\text{-}AC}$ can be calculated from measured ^{13}C NMR parameters and the ultimate analysis for a given coal, char, or tar sample, as follows:

$$R_{N-AC} = \frac{\%N}{\%C \cdot f_a'} \qquad (2)$$

where f_a' is the fraction of carbon atoms which are aromatic and %N and %C are the nitrogen and carbon weight percents on a dry ash-free (daf) basis in a coal or char sample. Since the value of AC_{cl} as calculated from ^{13}C NMR data typically contains a large degree of uncertainty, the variable $R_{N\text{-}AC}$ is used, since it is independent of the number of aromatic carbons per cluster.

In order to evaluate the adequacy of a first order rate expression with distributed activation energy in describing nitrogen release as light gas, a simple model was developed for comparison of actual changes in $R_{N\text{-}AC}$ during devolatilization for chars of various coals. This model is based on the same assumptions as the earlier models, but uses only three coal-independent parameters, which were adjusted to describe the average behavior of $R_{N\text{-}AC}$ in the chars of five coals during rapid devolatilization at 1250 K. In this model, the value of $R_{N\text{-}AC}$ is then assumed to decay as a first order process:

$$\frac{dR_{N-AC}}{dt} = -A_N \exp(-E_N / RT_p) \cdot R_{N-AC} \qquad (3)$$

where the activation energy (E_N) is distributed according to a normal probability distribution (with mean value of E_{0N} and a standard deviation of σ_N) as a function of the extent of $R_{N\text{-}AC}$ disappearance, in a manner similar to that used by Fletcher et al. (1992).

In order to correctly predict nitrogen release, devolatilization models must not only correctly predict tar and char yields, but must also correctly treat changes in the cluster molecular weight (MW_{cl}) and average cluster attachment molecular weight (MW_a) in the char. Since the nitrogen is contained only in the aromatic groups in the coal, a meaningful variable is the fraction of mass which is aromatic (f_a^{mass}). The %N in the char can then be calculated as follows:

$$\%N = R_{N-AC} \cdot R_{AC-AM} \cdot f_a^{mass} \tag{4}$$

where

$$f_a^{mass} = \frac{MW_{cl} - MW_a \cdot (\sigma + 1)}{MW_{cl}} \tag{5}$$

and

$$R_{AC-AM} = \frac{\%C \cdot f_a}{f_a^{mass}} \tag{6}$$

and $\sigma + 1$ is the average number of attachments per cluster. R_{AC-AM} is the ratio of aromatic carbon mass to the total aromatic mass in the char, which is assumed to remain constant during devolatilization. The nitrogen release is then calculated as follows:

$$NR = \frac{\%N_{coal} - f_{char} \cdot \%N_{char}}{\%N_{coal}} \tag{7}$$

where f_{char} is the daf char yield, as calculated by the devolatilization model. Thus, in order to correctly describe the chemistry of nitrogen release from char during devolatilization, a devolatilization model should correctly predict tar and char yields and f_a^{mass}, or an equivalent variable describing the char aromaticity.

Evaluation of Models

Devolatilization data reported by Fletcher and Hardesty (1992) were used for evaluation of the devolatilization model nitrogen release chemistry. They reported yields and ultimate analyses for the chars of five coals, entrained in nitrogen in an electrically-heated drop tube reactor for maximum gas temperatures of 1050 and 1250 K, and collected at various residence times. All of the coals and several of the chars for seven of the ten experimental conditions were also analyzed by ^{13}C NMR, giving quantitative details of the evolution of the chemical structure during rapid devolatilization for these coals. Particle temperature profiles were carefully measured, facilitating devolatilization model evaluation. Since yields and ultimate analyses of the tars were not reported for these data, evaluation of model predictions for nitrogen release to the tar were not possible.

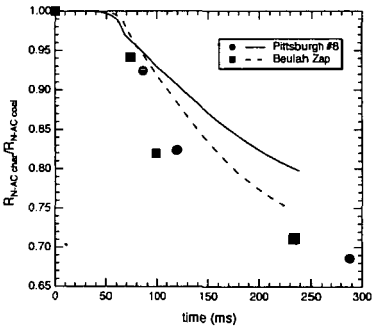

Figure 1. Comparison of predicted (lines) and measured (symbols) nitrogen to aromatic carbon ratios during rapid devolatilization at **1250 K** for the chars of three coals, normalized by the nitrogen per aromatic carbon ratio in the parent coal. R_{N-AC} decays more rapidly than average for these coals.

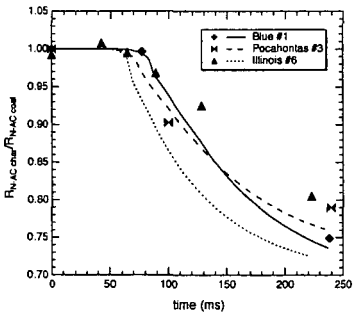

Figure 2. Comparison of predicted (lines) and measured (symbols) nitrogen to aromatic carbon ratios during rapid devolatilization at **1250 K** for the chars of two coals, normalized by the nitrogen per aromatic carbon ratio in the parent coal. R_{N-AC} decays more slowly than average for these coals.

To evaluate the use of a simple first order rate expression (Equation 3) to model nitrogen release to the light gas, three coal-independent constants were used. Values for the activation energy mean and deviation were taken to be 52 and 6 kcal/mol respectively for all coals (in a manner similar to Bassilakis et al., 1993) to describe HCN formation at both low and high heating rates. The pre-exponential factor was then varied to obtain the value which best modeled the changes in R_{N-AC} for the chars of all five coals during rapid devolatilization. A pre-exponential factor of $8.4 \times 10^8\ s^{-1}$ was found to adequately describe the decay of R_{N-AC} for all coals. In Figures 1-3, experimentally measured R_{N-AC} values in the char throughout devolatilization are compared with those predicted by the simple nitrogen release model, revealing an unmistakable bias by coal type. Since the particle temperature profiles were precisely measured for the devolatilization tests

discussed here, the biases in $R_{N\text{-}AC}$ behavior are not thought to be due to errors in the particle temperature profile. For some coals $R_{N\text{-}AC}$ decays consistently faster than the predicted values, and for other coals decaying consistently slower. What is more, the bias appears to change for some coals with changes in gas temperature.

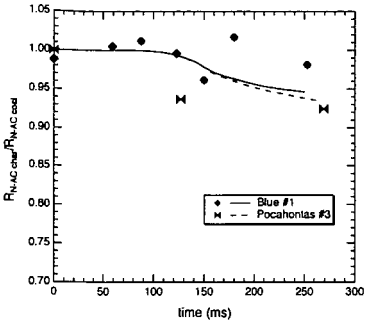

Figure 3. Comparison of predicted (lines)and measured (symbols) nitrogen to aromatic carbon ratios during rapid devolatilization at **1050** K for the chars of two coals, normalized by the nitrogen per aromatic carbon ratio in the parent coal.

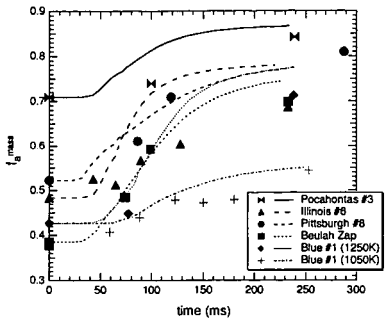

Figure 4. CPD predictions (lines) of f_a^{mass} compared with values as calculated from ^{13}C NMR analysis of coal chars produced during rapid devolatilization (symbols).

If reactivity is defined as the ease with which nitrogen is released as light gas during devolatilization, inspection of Figures 1 and 2 show that the order of HCN release reactivity for these five coals at 1250 K is Pittsburgh #8 > Beulah Zap > Blue #1 > Pocahontas #3 > Illinois #6. This order of reactivity does not correlate well with rank, nor does it seem to correlate with the O/N ratio. For the data available at 1050 K it appears that the order of reactivity is Pocahontas #3 > Blue #1. Thus Pocahontas #3 and Blue #1 appear to have different activation energies, the former releasing more rapidly than the latter at low temperature, and the latter releasing more rapidly than the former at high temperature .

Chemical Percolation Devolatilization (CPD) model predictions of f_a^{mass} during devolatilization are compared with the experimentally measured values in Figure 4. Except for Illinois #6, the predictions are quite good, generally deviating less than 4% (absolute) from the data.

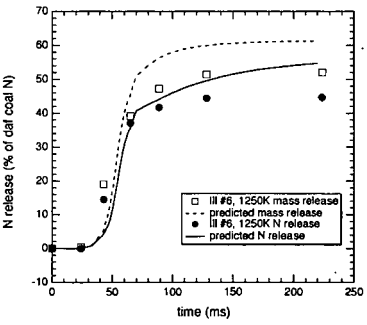

Figure 5. Predicted and measured mass and nitrogen release from 106-125μm PSOC 1493D Illinois #6 coal during rapid devolatilization at 1250 K in a drop tube reactor.

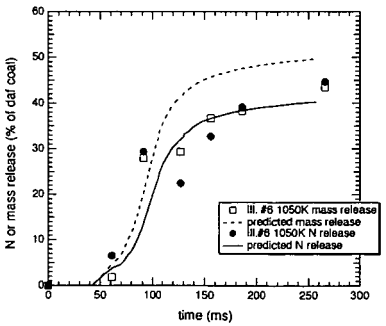

Figure 6. Predicted and measured mass and nitrogen release from 106-125μm PSOC 1493D Illinois #6 coal during rapid devolatilization at 1050 K in a drop tube reactor.

Using the CPD model for tar and total mass release predictions, the nitrogen release model (as described in the introduction) was evaluated against the data of Fletcher and Hardesty. Figures 5-12 compare the model predictions of nitrogen release as a fraction of daf coal nitrogen during rapid devolatilization against the experimentally measured nitrogen release for several coals. For the most part, the agreement is fairly good, except where mass release is incorrectly predicted. The mass release, as predicted by the CPD model, is also shown for reference, as the nitrogen release prediction depends directly on the predicted mass release according to Equation 6. In Figures 5 and 6, the nitrogen release is shown for devolatilization of Illinois #6 coal for two different gas

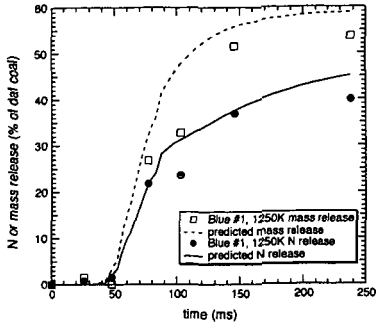

Figure 7. Predicted and measured mass and nitrogen release from 106-125μm PSOC 1445D Blue #1 coal during rapid devolatilization at 1250 K in a drop tube reactor.

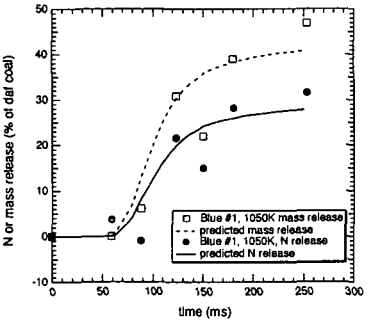

Figure 8. Predicted and measured mass and nitrogen release from 106-125μm PSOC 1445D Blue #1 coal during rapid devolatilization at 1050 K in a drop tube reactor.

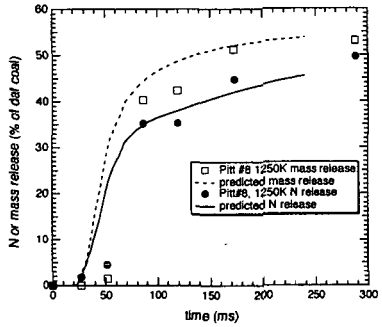

Figure 9. Predicted and measured mass and nitrogen release from 63-75μm PSOC 1451D Pittsburgh #8 coal during rapid devolatilization at 1250 K in a drop tube reactor.

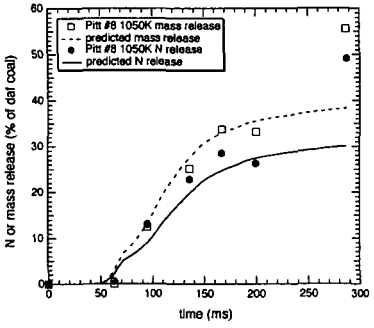

Figure 10. Predicted and measured mass and nitrogen release from 63-75μm PSOC 1451D Pittsburgh #8 coal during rapid devolatilization at 1050 K in a drop tube reactor.

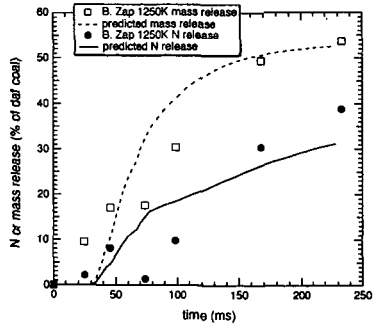

Figure 11. Predicted and measured mass and nitrogen release from 75-106μm PSOC 1507D Beulah Zap coal during rapid devolatilization at 1250 K in a drop tube reactor.

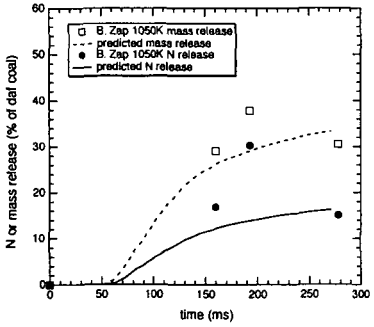

Figure 12. Predicted and measured mass and nitrogen release from 75-106μm PSOC 1507D Beulah Zap coal during rapid devolatilization at 1050 K in a drop tube reactor.

temperature profiles. The 1250 K chars for Illinois #6 seem to release very little nitrogen after 100 ms residence time. However, the experimentally measured nitrogen release at the 1050 K gas temperature condition continues to increase the entire 250 ms, eventually exceeding the level of mass release. This suggests that as much or more nitrogen was released as light gas at 1050 K than at 1250 K for Illinois #6 coal. On the other hand, Blue #1 (Figures 7 and 8) does not exhibit enhanced nitrogen release at the 1050 K condition, although the particle temperature is only 20 K cooler on average than that of the 1050 K Illinois #6 chars. This suggests a fundamental difference in the nitrogen release characteristics of the Blue #1 and Illinois #6 chars, which could possibly be due to differences in parent coal nitrogen functionality distribution. Such differences are not well modeled by a simple first-order rate expression with coal independent constants.

Conclusions

Nitrogen release models based on a dual mechanism of tar shuttling and nitrogen release from the char as light gas according to a first order rate expression with distributed activation energy can predict total nitrogen release fairly well. However, coal-dependent deviations from such a model are pronounced for the nitrogen release behavior during devolatilization. These deviations depend on coal type in a manner that seems to be independent of rank. Furthermore, the temperature dependence of the nitrogen release as light gas appears to vary from coal to coal. The reasons for these deviations are not well understood, but may be related to differences in char nitrogen functionality distribution.

Acknowledgemts

This work was funded in part by the New Energy and Industrial Technology Development Organization (NEDO) supervised by the Ministry of International Trade and Industry (MITI) of Japan, in collaboration with Professor Masakatsu Nomura at Osaka University. We also thank Dominic Genetti, Eric Hambly, and Todd Salisbury for many useful discussions.

References

Bassilakis, B., Y. Zhao, P. R. Solomon, and M. A. Serio "Sulfur and Nitrogen Evolution in the Argonne Coals: experiment and modeling," *Energy and Fuels*, **7**, 710-720 (1993).

Fletcher, T. H., A. R. Kerstein, R. J. Pugmire, M. S. Solum, and D. M. Grant, "Chemical Percolation Model for Devolatilization," *Energy and Fuels*, **6**, 414-431 (1992).

Fletcher, T. H. and Hardesty, D. R., "Compilation of Sandia Coal Devolatilization Data, Milestone Report, Milestone Report for DOE's Pittsburgh Energy Technology Center," contract FWP 0709, Sandia Report No. SAND92-8209, available NTIS (1992).

Niksa, S., "FLASHCHAIN Theory for rapid coal devolatilization kinetics. 6. Predicting the Evolution of Fuel Nitrogen from Various Coals," *Energy and Fuels*, **9**, 467-478, (1995).